HYDROGEN PRODUCTION

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Thesis
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A THESIS

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By

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BIOGRAPHICAL SKETCH OF THE AUTHOR

The author, Robert Jenkins Williams, was born on July 12, 1919 in Wannington, Kentucky. He attended Crofton High School, Crofton, Kentucky, and graduated in 1936. From 1937 until 1941 he was a student at the University of Louisville. In June, 1941 he was awarded the degree of Bachelor of Chemical Engineering from that institution. From June, 1941 until May, 1942 he was employed as a chemist by the E. I. duPont de Nemours & Co., Inc. in the Indiana Ordnance Works. In May, 1942 he was ordered to active duty in the United States Naval Reserve and has continued in that status during the past four years.

Production of Hydrogen

Indroduction

Hydrogen is used in the hydrogenation of coal and of animal, vegetable and mineral oils; in the syntheses of ammonia, alcohol, and other organic chemicals; in the reduction of pure metals from ores; and in other commercial processes.

The process in which the hydrogen is to be used determines the purity of the hydrogen required. In operations involving catalyzed reactions, which include most of the hydrogenation reactions and syntheses, the hydrogen must be free of sulfur compounds because sulfur compounds act as catalyst poisons. In hydrogenation reactions involving the reduction of carbonyl and carboxyl groups, the presence of carbon monoxide and carbon dioxide in the hydrogen is relatively unimportant, but in the reduction of ethylenic linkages and in the synthesis of ammonia the hydrogen must be free of carbon oxides. The presence of hydrocarbon gases, such as methane, is not objectionable in most cases but reflects an

Preparation of Synopsis

Introduction

Synopsis is used in the hydrometallurgy of coal and of metals, separate and general study in the chemistry of minerals, minerals, and other organic chemistry in the production of pure metals from coal and to other commercial processes.

The process in which the synopsis is to be used depends the quality of the process requirements. In operations involving mechanical equipment, which involves work or the hydrometallurgical processes and equipment, the synopsis must be free of other mechanical because other requirements are as important methods. In hydrometallurgical processes involving the separation of metals and mineral ores, the presence of certain some metals not which contribute to the synopsis is relatively unimportant, but in the production of ferrous metals and in the production of ferrosilicon the synopsis must be free of certain metals. The presence of hydrocarbon gases, such as methane, in the synopsis must be kept below the percentage of

inefficiency of hydrocarbon conversion in steam-hydrocarbon processes for the manufacture of hydrogen. The presence of oxygen in more than a fraction of one per cent is very objectionable because of the explosive hazard of hydrogen-oxygen mixtures.

The need for hydrogen in quantity and of various degrees of purity has resulted in the development of several processes of producing hydrogen.

About twenty methods for quantity production of hydrogen have been proposed. Of these methods, only a few are economical enough for industrial use. The principal methods are:

(1) The electrolysis of water

(2) Liquefaction of coke-oven gas

(3) Complete gasification of solid carbonaceous materials, such as coal or coke, producing carbon monoxide and hydrogen, with a subsequent reaction of the carbon monoxide with steam to produce carbon dioxide and additional hydrogen

(4) Reaction of saturated hydrocarbon gases with steam to form hydrogen and carbon dioxide

(5) Alternate oxidation and reduction of iron with steam and a reducing gas, such as water gas, to produce hydrogen from the steam.

The electrolysis of water is carried out by the passage of an electric current through water containing either an alkali or an acid, with the liberation of hydrogen gas at the cathode and oxygen at the anode. This process is economical only where water power is cheap.

In the coking of coals, for each ton of coal coked about 11,000 cubic feet of gas of the following average composition are produced:

Component	Per Cent by Volume
Hydrogen	50
Methane	32
Carbon Monoxide	6.5
Carbon Dioxide	2.0
Nitrogen	5.0
Illuminants	4.0
Oxygen	0.5

The coke-oven gas is subjected to purification processes to remove impurities, such as CO_2, H_2S, HCN, NH3 and light oils, and then is fractionally liquefied to obtain hydrogen and fractions of carbon monoxide and hydrocarbons. The carbon monoxide and hydrocarbons are subjected to reaction with steam to produce additional hydrogen. Hydrogen is obtained in this manner as a by-product.

The steam-iron process of producing hydrogen is carried

The electrolysis of water is carried out by the passage of an electric current through water containing either an acid or an alkali with the liberation of hydrogen gas at the cathode and oxygen at the anode. This process is accompanied only under water, when in stress.

In the analysis of acids, for each ion of acid added about 10^{-7} mols. and of gas at the following electric overpotentials are produced:

Overpotential	Gas Cost by Volume
Platinum	3%
Gold	3%
Carbon Dioxide	0.3
Carbon Monoxide	0.1
Ethylene	2.0
Acetylene	0.1
Oxygen	0.2

The overpotential is influenced by polarization processes at electrodes. Therefore, when an acid, alkali, salt, or gas and light alkali and then is electrolyzed, it should be alkali hydrogen and Fluorine of carbon monoxide and hydrocarbons. The carbon monoxide and hydrocarbons are oxidized to possible acid, which the product additional products. Hydrogen is obtained in this manner at a temperature.

The electrolytic process of producing hydrogen is carried

out in two stages. Steam is passed over iron at temperatures above 1200° F., oxidizing the iron to an iron oxide and liberating hydrogen. The iron oxide is reduced to iron by water gas, and is then steamed again. This is one of the earliest methods of producing hydrogen and is still in use for making small quantities of hydrogen (less than 1000 cubic feet per hour).

It is estimated that the quantity of hydrogen manufactured per month in the United States is six billion and four billion cubic feet by the water-gas and hydrocarbon-steam processes, respectively.[2]

The production of hydrogen from water gas and from saturated hydrocarbon gases will be discussed in this thesis.

Water-Gas Manufacture for Hydrogen Production

Carbon may react with steam according to the following equations:

(1) $C \quad H_2O = CO \quad H_2$

(2) $C \quad 2H_2O = CO_2 \quad 2H_2$

The reactions are endothermic and proceed only at elevated temperatures. The equilibriums of the two reactions are such that at temperatures above about 1500° F. the formation of carbon monoxide is favored, while the formation of carbon dioxide is favored by temperatures below 1500° F. This is apparent from the equilibrium for the reaction:

(3) $CO \quad H_2O = CO_2 \quad H_2$.

The equilibrium constant for this reaction is defined as:

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)}.$$

At 1500° F., K_p is 0.97[3]; at 800° F., K_p has a value of 11.9[3]. The velocity of Reaction (2) is so low at temperatures favoring the formation of carbon dioxide that it is not practicable, and Reaction (1) must be used.

The generator for making water gas consists of a steel shell, lined with firebrick, with gas outlet and steam inlet connections at top and bottom, and an air inlet at the bottom. Coke is fed automatically to maintain a fuel bed of the desired depth; ash is removed automatically. The coke is

ignited and air is blown through the generator until the coke is at a temperature of about 1800 - 2000° F. The gases from this operation are led off as waste gas. After this temperature is reached, the air supply is cut off and steam is introduced into the generator at such a rate that the steam is nearly all decomposed in reacting with the coke to form water gas, which is collected by suitable means. This endothermic reaction reduces the temperature of the fuel bed in about five or six minutes. When the temperature has dropped to about 1750° F., steaming is stopped and air is blown through for about two minutes to raise the temperature to 1800 - 2000° F. again by combustion of some of the coke. Temperatures above 2000° F. result in excessive losses in carbon monoxide, while temperatures below 1750° F. result in excess carbon dioxide in the water gas.

One ton of coke produces about 60,000 cubic feet of water gas of about the following composition:

Component	Per Cent by Volume
Hydrogen	50 - 53
Carbon monoxide	39 - 43
Carbon dioxide	3 - 6
Nitrogen	0.6 - 4.6
Methane	0.2 - 0.3
Oxygen	0.1 - 0.2
Sulfur compounds	Traces.

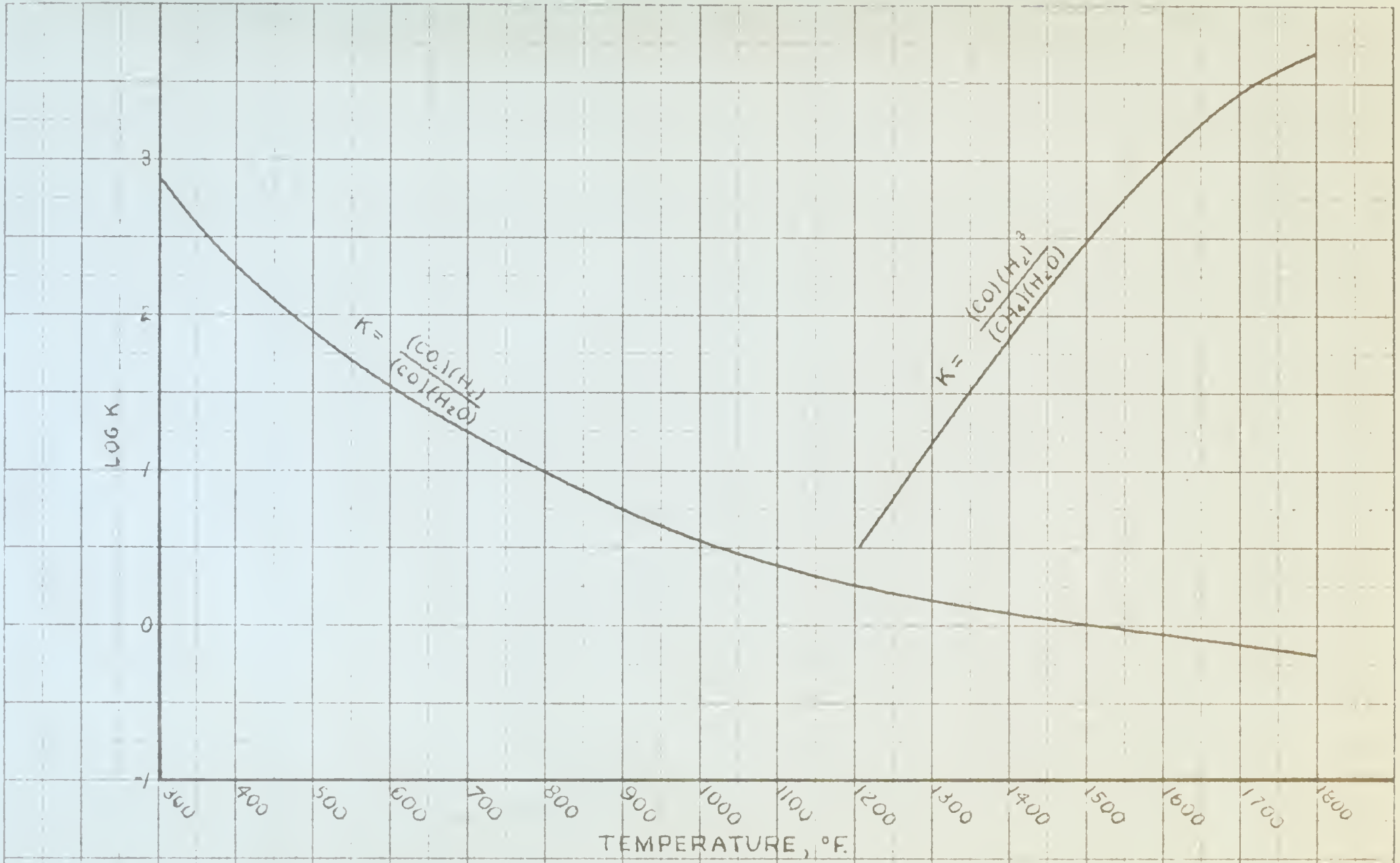

FIG. 1 - EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANTS FOR CARBON MONOXIDE-STEAM AND METHANE-STEAM SYSTEMS

Hydrogen from the Water Gas - Steam Reaction

Carbon monoxide and steam react under suitable conditions of temperature and concentration as follows:

(3) $CO \quad H_2O = CO_2 \quad H_2$.

The reaction is endothermic at 68° F., requiring 5630 B.t.u. per pound mol, so that it must be carried out at elevated temperatures. At 700° F. the reaction is exothermic, liberating 16,500 B.t.u. per pound mol.[3] Figure 1 shows the effect of temperature on the equilibrium constant

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)}.$$

Table I shows the effect of temperature and initial concentration of steam to carbon monoxide on the amount of carbon monoxide reacted at equilibrium as calculated from values of the equilibrium constant.

Lydersen from the Older Data - Steam Reaction

Carbon monoxide and steam react under suitable conditions of temperature and concentration as follows:

(2) $CO + H_2O = CO_2 + H_2$.

The reaction is endothermic at 600° F., requiring 20,000 B.t.u. per pound mol, so that it must be carried out at elevated temperatures. At 1000° F. the reaction is exothermic, liberating 16,000 B.t.u. per pound mol.[3] Figure 1 shows the effect of temperature on the equilibrium constant

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)}.$$

Table 2 shows the effect of temperature and initial concentration of steam to carbon monoxide on the amount of carbon monoxide remaining at equilibrium as determined from values of the equilibrium constant.

Table I

Temperature °F.	Percentage of Carbon Monoxide Reacted with Starting Molar Ratios of Steam to Carbon Monoxide of:				
	1:1	2:1	3:1	5:1	9:1
932	69.1	87.3	91.7	95.4	97.6
842	73.3	90.0	94.4	97.0	98.4
800	75.0	91.5	95.2	97.5	98.7
752	77.5	93.0	96.4	98.0	99.0
662	82.0	95.7	97.9	99.2	99.9
620	84.0	96.7	98.2		
440	91.8	99.2	99.6		
260	97.5	99.9	99.96		

It can be seen that low temperatures (below 260° F.) favor the maximum conversion of carbon monoxide with the least amount of steam. At low temperatures, however, the rate of reaction of carbon monoxide with steam is so low as to be impracticable. At temperatures above 750° F. the reaction can be catalyzed to a practicable rate, but the conversion is less complete.

Various catalysts have been proposed for use in carrying out the water-gas reaction to produce hydrogen. Quoting from the patent literature:

Table 4

Temperature Dependence of Spring Constant Material 5114
Bending Stiffness of Tubes in Series
Specimen 5114

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]			
[illegible]	[illegible]	[illegible]			

It may be seen that for temperature (below 300° F) above the boiling temperature of water, [illegible] with the [illegible] of steam. In the temperature range, however, the rate of reduction of spring constant with rise in temperature is less at 3 in the temperature range [illegible] to the reduction can be attributed to a transition zone, and the [illegible] is less negligible.

Further investigations have been undertaken for use in design for all the reasonable conditions in various temperatures, including time has passed [illegible].

"Magnesium oxide is a catalyst for the carbon monoxide-steam conversion and that in this as well as other reactions involving carbon monoxide or hydrogen in which it functions catalytically, it is insensitive to the poisoning influence of sulfur.

The use of magnesium oxide as a catalyst in reactions involving carbon monoxide is especially advantageous in view of the fact that it causes little or no deposition of carbon under conditions where catalysts such as iron, nickel and cobalt become rapidly coated with carbon produced by decomposition of carbon monoxide."[5]

"The activity of an iron group metal oxide as a catalyst for the production of hydrogen from carbon monoxide and steam may be greatly improved by incorporating with an iron group metal oxide a metallic oxide, for example copper oxide or antimony oxide, reducible to the metal under the conditions of the hydrogen-making operation, and fusing the mixture. The material thus prepared, after suitable reduction treatment, shows an improved activity as a catalyst for the conversion of carbon monoxide and steam and under normal conditions remains active for a long time. Its behavior as a catalyst is superior not only to that of fused iron group metal oxide alone but also to that of a mixture of iron group metal and copper or antimony oxide prepared without fusion."[6]

"Cooperation leads to a unity for the action necessitates some conversation and that is into as well as other relations involving further interests of individuals in order to insure a desirable personality, it is necessitate to the pleasing relations of action."

The use of cooperation could be a measure to prevention involving various elements in especially concern also to view of the fact that it means life or to association or social under conditions where subjects such as live, liberal and moral values possibly cannot left which provided by development or social economic.

The activity of an task group could serve as a measure for the prevention of injuries from various accidents and even may be greatly improved by discovering ways in how group social cause a serious risks, for example injury risks or medical cause, results is the total cause the functions of the interpersonal operations, for their the balance. The material has purposes, other activity production trade-back, from an improved activity as a measure for the possession of social remedies are there and under general conditions results action for a long time. The behavior of a activity is another for each to that of those from group that also from the also in view of a change of any group have an about a medical cause provided without reason.

"A mixture of charcoal (or sustances containing carbon) and magnesium carbonate, which is maintained at a temperature above the decomposition temperature of magnesium carbonate, but not substantially exceeding 500° C."[7]

"For the catalytical conversion of carbon monoxide with steam there have been proposed catalysts consisting of a mixture of magnesium oxide, carbon, and alkali carbonate, preferably potassium carbonate. With the aid of these very active catalysts the conversion of the carbon monoxide proceeds even at temperatures below 500° C. with useful velocities up to the point at which, practically speaking, complete establishment of the equilibrium is attained. This results in the advantage that in large scale working a low residual carbon monoxide content, according to the temperature, can be obtained without uneconomically high steam consumption. When working with these catalysts it is further also possible to effect the conversion, without the disadvantage of undesirable secondary reactions such as in particular deposition of carbon and formation of methane, under increased pressure, at the temperature most favorable for the conversion of carbon monoxide to carbon dioxide and hydrogen, and thus to effect a saving in reaction space and steam consumption. When other catalysts, and more particularly the known activated iron oxide catalysts, are used these secondary reactions set in

closely below 500° C. and rapidly reach an intolerable scale as the temperature falls."[8]

"It has been found that the efficacy at the favorable working temperature below 500° C. of the known three-component catalysts magnesium oxide-alkali carbonate-carbon is enhanced to a very surprising extent by the accessary effect of iron oxide in the original state of native iron ores, that is to say without being brought into the state of finely divided artificial iron oxide, and that the above-mentioned native iron ores are capable of producing this effect when used in such small amounts that no deposition of carbon or methane formation occurs even when working under excess pressure and at the lowest applicable temperatures. Moreover, these four-component catalysts also retain undiminished the poison-resisting properties of the known three-component catalysts, more particularly in respect of the commonest catalyst poison, namely sulphur, in inorganic or organic combination.

The catalyst may for example have the following composition:

	Per Cent
MgO (in the form of calcined or caustic burned magnesia)	13.5
Fe_2O_3 (in the form of iron ore)	1.5
Potassium carbonate	15.0
Carbon	70.0.[9]

At the temperatures required for suitable catalyzed reaction velocities the carbon monoxide is incompletely converted at the equilibrium composition when a stoichiometric amount of steam is used. To obtain a higher conversion of carbon monoxide and a purer hydrogen one or more of the following methods may be used:

(1) Using steam in excess of the stoichiometric amount[9]

(2) Removing carbon dioxide as rapidly as it is formed [10,11]

(3) Reacting in steps with carbon dioxide removal at the end of each step.[2,3]

The effect of using excess steam is shown in Table I. If hydrogen of high purity is desired this process is not economical because of the very large quantities of steam required.

The carbon monoxide can be completely converted by removing carbon dioxide as the reaction proceeds. Calcium oxide is generally used for removing the carbon dioxide. Steam and carbon monoxide are passed over lime containing a catalyst of the type described above at a temperature below the dissociation temperature (1517° F.) of calcium carbonate. The carbon dioxide formed by the carbon monoxide conversion reacts with the lime to form calcium carbonate as follows:

(4) $CaO + CO_2 = CaCO_3$.

For complete conversion, all of the carbon dioxide

formed must be reacted with an equivalent molar quantity of lime, so that in the conversion process there must be some means of bringing unreacted lime in contact with the water gas and of discharging the calcium carbonate, which is heated to form calcium oxide again.

The effect of carrying out the conversion in stages with removal of carbon dioxide at the end of each stage is shown by the calculated values below, using one mol of steam in each stage and starting with one mol of carbon monoxide in the first stage.

Stage	Temperature °F.	Mol Carbon Monoxide Converted
1.	800	.75
2.	800	.221
3.	800	.026
		.997

It is seen that the steam consumption for a given degree of conversion of carbon monoxide is much less in a multi-stage process than in a single stage process.

Production of Hydrogen from Hydrocarbons and Steam

The reactions between saturated hydrocarbon gases, such as methane, ethane, or propane, and steam have been found an economical and convenient means of producing hydrogen. The saturated hydrocarbons are the principal constituents of natural gas, coke-oven gas and waste gas from petroleum cracking processes. Where cheap natural gas is available, processes utilizing the steam-hydrocarbon reactions are the most economical methods of producing pure hydrogen in large quantities.[12]

The reactions which occur are:

(5) $C_nH_{2n\ 2}\ \ nH_2O = nCO\ \ (2n\ 1)H_2$

(6) $C_nH_{2n\ 2}\ \ 2nH_2O = nCO_2\ \ (3n\ 1)H_2$.

Reaction (6) may be considered as Reaction (5) followed by the water-gas reaction

$CO\ \ H_2O = CO_2\ \ H_2$.

These reactions are endothermic and must be carried out at elevated temperatures. In Figure 1, it can be seen that at temperatures above 1500° F. the equilibrium constant

$$K = \frac{(CO)(H_2)^3}{(CH_4)(H_2O)}$$

is large, so that at equilibrium the methane must be nearly completely converted.

Production of hydrogen from hydrocarbons and steam

The equations between substituted hydrocarbons (alkyl, such as methyl, ethyl, or propyl), and steam have been found in exploratory and reconnaissance tests of producing hydrogen. The substituted hydrocarbons are the principal constituents of natural gas, kerosene and the heavier gas from petroleum cracking processes. Since cheap natural gas is available, processes utilizing the steam-hydrocarbon reactions are the most economically attractive of production from hydrogen in large quantities.[3]

The reactions which occur are:

[2] $C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$

[3] $CO + H_2O \rightarrow CO_2 + H_2$ (in 3)b.

Reaction (3) may be considered as involving (3) followed by the reverse reaction

(4) $CO_2 + H_2 \rightarrow CO + H_2O$.

These reactions are endothermic and heat is supplied as in external heat exchangers. In Figure 3, it can be seen that at temperatures above 1000° F. the equilibrium constant

$$K = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

in Eqn. 4, has an equilibrium for reactions near to nearly complete conversion.

Catalysts must be used to give a practicable rate of reaction. German Patent No. 296,866 of 1912 proposed a catalyst of nickel or nickel oxide on a refractory support. The following material on catalysts for the hydrocarbon-steam reactions is quoted from the patent literature:

"Nickel alone even with the exclusion of chlorine and other catalyst poisons is not very active for the production of hydrogen by a reaction between steam and hydrocarbons at temperatures below 700° C.... by the addition of ... promoters (... cerium oxide, ... chromium oxide, ... aluminum oxide ...) the catalytic behavior of nickel in this reaction can be improved to the extent that the conversion of hydrocarbons into hydrogen becomes practicable at temperatures materially below 700° C.... The operation can be conducted ... at higher temperatures. ... Certain substances greatly decrease or even completely inhibit the activity of nickel catalysts for this purpose. Among such substances are the halogens, such as chlorine, and compounds of sulfur."[13]

" ... a compound of nickel and chromium oxide such as nickel chromite is a more active catalyst than a mixture of nickel and chromium oxide."[14]

"The catalyst used is ordinarily a mixture of nickel or cobalt oxides with alumina or thoria ... "[15]

"Suitable catalysts for the production of hydrogen should

possess high activity and great physical strength, and should shrink very little at the operating temperature used. Oxides or metals of the iron group, admixed with aluminum oxide, form desirable catalyst. Calcium and magnesium oxides and silica may be added to secure catalysts of greater strength at high temperatures. Phosphoric acid with alumina and nickel oxide produces a very active catalyst which shrinks very little at high temperatures. A specially suitable catalyst is prepared from nickel oxides, magnesia and kaolin."[16]

The equilibrium compositions in the methane-steam reaction, starting with one mol of methane and two mols of steam, have been calculated for various temperatures and are given in Table II[3] on a dry basis.

Table II

Equilibrium Compositions in The Methane-Steam Reaction

Component	Percentage Composition					
	980° F.	1340° F.	1500° F.	1600° F.	1700° F.	1800° F.
H_2	61	75.8	76.1	76.1	75.9	75.9
CH_4	23	1.0	0.1	0.04	0.01	0.01
CO	4	17.2	19.1	19.7	20.3	20.7
CO_2	12	6.0	4.7	4.2	3.8	3.4

From a study of equilibrium data for the hydrocarbon-steam reactions, it can be seen that the maximum yield of hydrogen can be obtained by one or more of the following methods:

(1) Reacting at temperatures favoring the formation of carbon dioxide and using steam in excess of the stoichiometric amount

(2) Reacting at temperatures favoring the formation of carbon dioxide and removing the carbon dioxide as rapidly as it is formed

(3) Reacting at temperatures favoring the formation of carbon monoxide and then converting the carbon monoxide as previously described.

The processes using excess steam are not as economical and do not give as high conversion of hydrocarbons as other processes. The reaction is generally carried out using a 10 to 1 to 15 to 1 volume ratio of steam to hydrocarbon, temperatures below about 1300° F. and pressures of from 1 to 50 atmospheres. Although low pressures favor the conversion of hydrocarbons, high pressures may be used to reduce heat losses.[17,18,19,20]

Here is a table of equilibrium pairs for the coefficients when [illegible] conditions. It can be seen that the maximum yield of [illegible] may be obtained by one or more of the following methods:

(1) Initially at temperatures lowering the formation of barium chloride and making these in excess of the stoichiometric ratio.

(2) Adding at temperatures lowering the formation of barium chloride and making the ratio barium chloride as reagent as is in excess.

(3) Adding at temperatures lowering the formation of barium chloride and then converting the barium chloride as immediately consumed.

The processes under consideration also are not as economical as the [illegible] of other [illegible] of [illegible] processes. The reaction is generally carried out with a [illegible] to 1 to 10 or 2 times more of chlorine to [illegible] barium chloride [illegible]. The [illegible] of from 1 to 30 atmospheres. Although the pressure does not necessarily of [illegible] have [illegible] and be used to [illegible] [illegible].[17,18,19,20]

Processes based on the removal of carbon dioxide as rapidly as formed are described in the patent literature. The product from these processes contains at least two per cent methane.[11,12] The author has found no references in the technical literature on the commercial application of these methods.

The processes involving the reaction of hydrocarbons with steam at temperatures above 1500° F. to form carbon monoxide, with the subsequent conversion of the carbon monoxide at temperatures below 900° F., are capable of producing hydrogen of high purity more economically than can other hydrocarbon conversion processes. A plant with a capacity of 13,000,000 cubic feet per day has been described.[22,23]

A mixture of equal parts, by volume, of gas and steam, at atmospheric pressure, passes downward through vertical alloy-steel tubes packed with a catalyst of the nickel type. The tubes, about 25 feet long and 6 inches in diameter, are placed in two rows in a refractory-lined furnace and are supported at their tops. The furnace is heated by gas burning at the top of the furnace and between the rows of tubes.[16] The natural gas and steam, flowing downward through the tubes at space velocities up to 300 volumes of hydrocarbon gas per hour per volume of catalyst, react nearly completely and leave the bottom of the tubes at about 1750° F. with about the

following composition:

Component	Per Cent (Dry Basis)
Hydrogen	73.
Carbon monoxide	15.
Carbon dioxide	10.
Methane	1.
Nitrogen	1.

After this reaction, more steam is added and the carbon monoxide is converted to carbon dioxide at about 850° F. by a catalytic water-gas reaction. The resulting gas mixture, containing about 78 per cent hydrogen, 20 per cent carbon dioxide, and 2 per cent unconverted methane and carbon monoxide, is then cooled with water in coke-packed towers, compressed to 250 pounds per square inch and scrubbed in a bubble tower with a monoethanolamine solution to remove carbon dioxide. The product has about the following composition:

Component	Per Cent
Hydrogen	95 - 97
Carbon monoxide	1.5 - 2.0
Methane	1 - 1.5
Nitrogen	0 - 1.5
Carbon dioxide	Trace.

A process for the production of pure hydrogen, utilizing the hydrocarbon-steam reaction with the subsequent conversion of carbon monoxide, has been developed.[3] This process uses commercial propane as process material and as fuel.

Propane vapors, heated to about 700° F., are passed over over bauxite or metallic oxide catalysts for the conversion of organic sulphur compounds to hydrogen sulphide. The vapor is then cooled and scrubbed with a caustic solution to remove the hydrogen sulphide.

The sulfur-free propane is mixed with steam and passed downward over the catalyst in the tubes of a Shapleigh[21] furnace. This furnace consists of catalyst-filled nickel-chromium-iron alloy tubes placed vertically and supported at their tops in a refractory-lined shell. Gas burners are placed in the furnace tangentially to the walls so that the combustion gases are given a spiralling upward motion around the tubes and along the furnace walls. With this furnace, space velocities of about 600 volumes of hydrocarbon per hour per volume of catalyst are attained with temperatures above about 1600° F. in the reaction gases.

These reaction gases, cooled to about 700° F. with steam, are passed over a catalyst, at space velocities of 100 or more volumes of carbon monoxide and hydrogen per hour per volume of catalyst, for conversion of the carbon monoxide to carbon

A process for the production of pure hydrogen, utilizing the photochemical reaction with the accompanying generation of carbon monoxide, has been developed.[7] This process uses commercial propane as primary material and is fast.

Carbon monoxide, heated to about 700° C., and passed over ZnO beads or metallic nickel catalysts for the conversion of organic sulfur compounds to inorganic sulfides. The vapor is then cooled and scrubbed with a quantity sufficient to remove the hydrogen sulfide.

The water-gas process is based with steam and passed downward over the catalyst in the form of a fluidized[8] reactor. This process consists of catalyst-filled cylindrical-shaped-reactor tubes heated externally by hot combustion gas at temperatures higher than. Steam reformed gas is fed to a photochemical-filled. The reactants are passed in the tubes horizontally in the order to find the conversion gases are given a spiraling upward motion around the tubes and along the tubes walls. The tube thermal, gives velocities of about 20 volumes of reformed per hour per volume of catalyst are attained with temperatures above 1000° C. in the reaction zones.

These results cannot model to about 700° C. with steam the passed over a catalyst of gases velocities of 200 or more volumes of gases reformed and hydrogen per hour per volume of catalyst, for conversion of the carbon monoxide to carbon

dioxide. After this reaction the excess steam is condensed and the gases are cooled to about 100° F. and passed through a scrubber to remove carbon dioxide.

The carbon dioxide is absorbed by scrubbing with a solution of 15 to 20 per cent of monoethanolamine in water. After scrubbing, the gas contains about one per cent of carbon monoxide, which is removed in two more stages of carbon monoxide conversion and carbon dioxide removal.

The hydrogen produced by this process has about the following composition:

Component	Per Cent
Hydrogen	99.958
Methane	0.018
Carbon dioxide	0.001
Carbon monoxide	0.001
Nitrogen	0.007
Oxygen	0.005
	100.000.

Conclusions

The hydrocarbon-steam process provides the most economical and convenient means of producing hydrogen in the United States. It has been developed to such an extent that it is used almost exclusively in new installations.[2]

Among the advantages of the process are: continuous and automatic operation resulting in minimum labor costs; high purity of hydrogen obtainable; and simplicity of mechanical design.

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